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Selectivity in bromination of aromatic substrates by molecular bromine in the presence of reusable zeolites

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Bromination of aromatic substrates, namely, toluene, phenol, phenyl acetate and chlorobenzene has resulted predominantly in the formation of para bromo derivatives. While solution bromination of phenyl acetate and chlorobenzene is very slow, zeolite-mediated bromination proceeds smoothly, reflecting the catalytic activity of zeolite in this reaction. A suitable mechanism involving assistance from the sodium ion in generating the active brominating species is proposed. The paraselective bromination of these substrates is also compared with that of nitration and the observed differences are suitably explained.

KEY WORDS: aromatic substrates; bromination; para selectivity; zeolites.

1. Introduction

Production of haloaromatics has long been a prominent industry, which also has associated problems such as selectivity, waste acid generation and considerable overreaction. This necessitates the use of efficient reagents with cleaner methodologies coupled with higher selectivities. Owing to the considerable emphasis on environmental impact of industrial chemical technologies [1], zeolites find extensive applications in recent years as catalysts for organic reactions [2–4]. Zeolite catalysis is also fast expanding into areas of speciality and fine chemicals' synthesis [5]. Recently, zeolites functionalized with transition metal complexes are found to be very efficient catalysts for selective organic transformations [6,7].

The needs for environmental safety and cleanliness are particularly acute in the field of electrophilic aromatic substitutions [8], which are poorly regioselective, may produce polysubstituted products and often require large quantities of hazardous Lewis acids. In this context, zinc bromide supported on mesoporous silica (or) acid-activated montmorillonite has been used as a fast, efficient, selective and reusable catalyst for the para bromination of activated and moderately activated aromatic substrates, with limited improvement in selectivity [9]. Recently, *in situ* generated bromonium ion from LiBr and ceric ammonium nitrate was employed [10] for the chemo- and regioselective oxidative nuclear bromination of activated aromatic compounds.

The role of zeolite catalysts in halogenation reactions has been reviewed [11]. Selectivities in chlorination of toluene by sulfuryl chloride [12] and of 4-chlorotoluene by ferric chloride [13] in the presence of zeolite catalysts have also been reported. Singh *et al.* [14] have studied the liquid-phase bromination of chlorobenzene, toluene and xylenes (*o*-, *m*- and *p*-) catalyzed by zeolites with *N*-bromosuccinimide as the brominating agent. Bromination in the presence of a zeolite can also be carried out with the molecular bromine [15] and the absence of any paraselectivity has been attributed to the formation of HBr. Sasson *et al.* [16] have overcome the drawback using epoxide as HBr scavenger and achieved a 98 : 2 selectivity in favor of the para isomer, though the conversion was around only 10%. Smith *et al.* [17], by varying the amount of the zeolite, have achieved a much more improved selectivity with higher conversion. According to them, with lower quantities of zeolite, the reaction consists of two separate components. In the first, NaY catalyzes the selective bromination, and in the subsequent second step, the HY zeolite formed acts as a less selective catalyst.

High paraselectivity can also be achieved in bromination of toluene by the use of *tert*-butyl hypobromite [18] as reagent and HNaX zeolite as catalyst in a solvent mixture comprising dimethyl ether and tetrachloromethane, but the reaction is not general.

However, most of the earlier studies of bromination concentrate on toluene (a weakly activated aromatic substrate) and detailed studies are desirable with the other activated/deactivated aromatic substrates. Also, many of them employ a polar solvent such as acetonitrile/dichloromethane, which tends to occupy the cavity, thus retaining the substrate in the solvent phase rather than in the interior of the zeolite cages. We have reported [19] recently the regioselective nitration of phenol inside the cages of zeolite using fuming nitric acid and a remarkable orthoselectivity is observed in this solid-state nitration. However, the regioselectivity is less

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significant in toluene and chlorobenzene, where zeolites normally favor para nitration [20]. This dichotomy in nitration reactions coupled with our interest in achieving selectivity in study of thermal and photochemical reactions in zeolite media [21–24] have prompted investigation of bromination of toluene, phenol, phenyl acetate and chlorobenzene (substrates of varying degrees of activation/deactivation in the aromatic ring) in a zeolite environment and the salient features are discussed below.

2. Experimental

2.1. Materials

Toluene, phenol and chlorobenzene (E-Merck) were employed without further purification. Faujasite NaY zeolite was obtained from Aldrich; molecular sieve 5A was obtained from E-Merck. The cations of interest were exchanged into the NaY powder by stirring with the corresponding nitrate solution (10%) at 70 °C for about 12 h. The exchange was repeated at least four times. Each time after exchange, the zeolite powder was washed repeatedly with distilled water and then dried. All the zeolites were preheated to 500 °C in a muffle furnace for 6 h before use.

2.2. Zeolite-catalyzed bromination of toluene (I), phenol (II) and chlorobenzene (III) in hexane slurry

The aromatic substrates (84 mmol) and the preheated zeolite (500 mg) were mixed in 4 mL hexane (hplc grade) and stirred together for 30 min. A known volume of bromine (94 mmol) dissolved in 1 mL hexane was added dropwise over 15 min at room temperature. After the addition was over, the mixture was stirred for an additional 45 min. The hexane portion was removed and the zeolite was subjected to overnight extraction with dichloromethane and filtered. The dichloromethane portion was mixed with the hexane portion and then analyzed by GC.

2.3. Solid-state bromination

The aromatic substrates (84 mmol) and preheated zeolites were stirred in 5 mL of hexane for 1 h at room temperature and allowed to settle. The hexane portion was removed and the solid portion was washed with 2 mL of hexane. The solid was dried in air for 2–3 min, and then a slow stream of nitrogen gas was passed through it for 5 min, followed by the addition of a known amount of bromine (94 mmol). The solid sample was kept at room temperature for an additional 45 min, extracted with dichloromethane (overnight) and then analyzed by GC.

2.4. Bromination of phenyl acetate (IV)

Phenyl acetate (1 mmol), the appropriate zeolite (0.5 g) and hexane (5 mL) were mixed in a round-bottomed flask fitted with calcium chloride guard tube and protected from light. The mixture was stirred at room temperature for 15 min, after which bromine (1 mmol) was added dropwise over 30 min while being stirred, and the stirring was continued for an additional 2.5 h. The reaction mixture was filtered and the solid was rapidly washed with acetone. An aqueous sodium hydrogen sulfite solution (10%, 10 mL) was quickly added to the filtrate to remove bromine and hydrogen bromide. The organic layer was washed with distilled water (30 mL), dried over anhydrous magnesium sulfate and then filtered.

The residual solid was then extracted with dichloromethane (25 mL) and the combined organic layers were subjected to GC analysis.

2.5. Analysis of the reaction mixture

All GC analysis was carried out on a Shimadzu 17A model gas chromatograph (with SE-30 10% capillary column, FID, high purity nitrogen as the carrier gas). Retention times of starting materials were taken as the internal reference. Products were identified by their retention time and also by coinjection with authentic samples. In all the cases the recovered mass balance was about 90%.

2.6. Spectral data of products

In many cases, products were isolated from the reaction mixture carried out in bulk. They were identified by their GC-retention time and also by their ^{1}H-NMR spectra (VI, VII and XI with a 90-MHz Perkin–Elmer instrument and the rest in a 300-MHz Bruker instrument). Measurements were made in $CDCl_3$ with TMS as an internal reference.

(VI) 7.1–7.2 δ (d, 2H), 6.7–6.8 δ (d, 2H) (AB pattern), 2.2 δ (s, 3H)

(VII) 7.1 δ (m, 3H), 6.7–6.8 δ (d, 2H), 4.3 δ (s, 2H)

(VIII) 7.3–7.4 δ (t, 1H), 7.1–7.2 δ (d, 1H), 6.9–7.0 δ (t, 1H), 6.7–6.8 δ (d, 1H), 5.5 δ (broad, 1H)

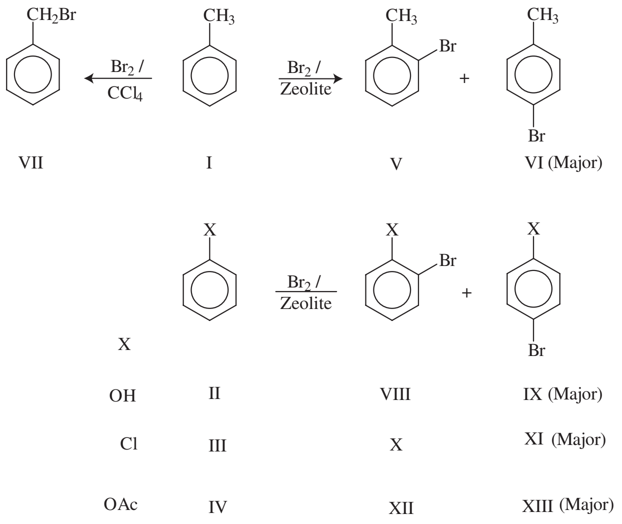
(IX) 7.3 δ (d, 2H), 6.7 δ (d, 2H) (AB pattern), 5.7 δ (broad, 1H)

(XI) 7.3 δ (d, 2H), 7.0 δ (d, 2H) (AB pattern)

(XIII) 7.4 δ (d, 2H), 6.9 δ (d, 2H) (AB pattern), 2.3 δ (s, 3H)

3. Results and discussion

In the present study, bromination of toluene, phenol, phenyl acetate and chlorobenzene were carried out using Br_2 dissolved in CCl_4, both in the presence and the



Scheme 1. Zeolite-assisted bromination of aromatic substrates.

absence of zeolites. The structures of the different products obtained are given in scheme 1. Hplc grade hexane (nonpolar) was employed as a medium of bromination with a view to ensure that the substrate was predominantly inside the zeolite cage. Control experiments show that there is no reaction between bromine and hexane under the experimental conditions.

In contrast to an earlier report [24] on solution bromination carried out in dichloromethane solvent (which produces benzyl bromide as the exclusive product), the zeolite-mediated bromination of toluene in the present study (presented in table 1) produced predominantly para-bromotoluene. Variation in cation size (as in KY and RbY) did not alter the product distribution. Use of acidic zeolites such as HY and CaY resulted in a significant amount of the ortho isomer, in addition to the para isomer, which was still the major product. Similarly, bromination in the solid state and also in the presence of NaX resulted in an almost exclusive para isomer formation. However, bromination with unactivated zeolite produced predominant side-chain bromination analogous to solution-phase bromination.

In the case of bromination of phenol also, bromination in the absence of zeolite yields para-bromophenol predominantly with a small amount of the ortho isomer. Carrying out the reaction in the presence of NaY, while markedly improving the percentage conversion, did not alter the product selectivity (table 2). Here also, as in the bromination of toluene, variations in the amount of zeolite, bromination with acidic zeolite HY and CaY, and solid-state bromination do not result in any variation in the yield of para isomer. Compared to toluene bromination, the amount of ortho isomer produced in phenol is more, reflecting the greater activation and hence the reactivity of the aryl ring in the latter. This behavior in bromination of phenol is in striking contrast to another closely related reaction namely, nitration, where the ortho isomer is the exclusive product [19] in the solid-state bromination. This difference in behavior points out that the two aromatic substitution reactions proceed differently in the presence of zeolites.

The zeolite-mediated bromination has also been extended to phenyl acetate. Unlike the previous two cases, there is no bromination reaction in solution in the absence of zeolite (table 3) and this is attributed to the deactivation of the aryl ring by the ester group. The zeolite-mediated bromination resulted in the predominant formation of para isomer. Changing the cation size, charge as well as acidity did not alter significantly the product distribution. However, the conversion was very poor with acidic zeolites HY, NiY and CaY. The yield was also very low with zeolites containing cations

Table 1
Percentage conversion and product distribution in bromination of toluene[a]

Solvent	Zeolite	% conversion	% yield of			
			V[b]	VI[b]	VII[b]	A[c]
CH_2Cl_2	nil	90	–	–	100	–
CH_2Cl_2	NaY	95	–	93	–	7
CH_2Cl_2	NaY[d]	100	–	–	80	20
Hexane	NaY	82	6	94	–	–
Hexane	HY	100	26	58	–	16
Hexane	NaX	100	–	90	–	10
Hexane	CaY	66	13	76	1	10
Hexane	KY	96	7	93	–	–
Hexane	RbY	100	5	95	–	–
–	NaY[e]	100	–	98	–	2

[a] Carried out at room temperature with 45-min stirring; analyzed by **GC**; error limit ± 2%.
[b] For structures of V, VI and VII, refer to scheme 1.
[c] Unidentified products.
[d] Reaction carried out with unactivated zeolite.
[e] Solid-state bromination.

Table 2
Percentage conversion and product distribution in bromination of phenol[a]

Solvent	Zeolite	$Br_2 \times 10^{-2}$ (mmol)	% conversion	% yield of		
				VIII[b]	IX[b]	A[c]
CH_2Cl_2	nil	0.94	35	19	81	–
CH_2Cl_2	NaY	0.94	80	10	80	10
Hexane	NaY[d]	0.94	48	12	84	4
Hexane	NaY	1.4	46	15	85	–
Hexane	NaY	0.94	86	4	81	15
Hexane	NaY[e]	0.94	77	3	58	39
Hexane	NaY[e]	0.47	61	–	73	27
Hexane	HY	0.94	61	12	81	7
Hexane	CaY	0.94	72	11	83	6
Hexane	RbY	0.94	78	4	85	8
Hexane	NaX	0.94	82	12	84	4

[a] Carried out at room temperature with 45-min stirring; analyzed by GC; error limit ± 2%.
[b] For structures of VIII and IX, refer to scheme 1.
[c] Unidentified products.
[d] Reaction carried out with unactivated zeolite.
[e] Solid-state bromination.

of larger size (BaY, CsY, RbY etc.). Bromination was also carried out at two different loading levels of the substrate and also in solid state, and once again the para bromo derivative was the major product. Similar selectivity has been observed previously [25].

With chlorobenzene also, solution bromination did not yield any product and the reaction was very very slow. This is in accordance with the deactivating nature of the chloro group. However, zeolite-mediated bromination produced predominantly para-bromochlorobenzene and the reaction was also faster. NaY was the zeolite of choice for this paraselective bromination. Here also, results similar to bromination of phenyl acetate were observed. Acidic zeolites such as HY and CaY decreased the rate of bromination. Similarly, zeolites with bulkier cations showed a decrease in percentage conversion.

The salient features observed in the present study are the following:

1. Catalysis of bromination by zeolites (even with deactivated aryl rings as in III and IV, bromination proceeds smoothly, while in the corresponding solution-phase bromination, there is no reaction).

Table 3
Percentage conversion and product distribution in bromination of phenyl acetate[a]

Solvent	Zeolite	% conversion	% yield of		
			XII[b]	XIII[b]	A[c]
CH_2Cl_2	nil	nil	–	–	–
Hexane	nil	nil	–	–	–
CH_2Cl_2	NaY[d]	68	–	100	–
Hexane	NaY	35	13	87	–
Hexane	NaY[e]	92	6.0	94	–
Hexane	CaY	6.0	20	16	64
Hexane	NaX	15	7.0	93	–
Hexane	CsX	4.0	–	90	10
Hexane	RbY	8.0	–	100	–
Hexane	BaY	nil	–	–	–
Hexane	NiY	20	10	68	22
Hexane	HY	nil	–	–	–
Hexane	NaY[f]	71	1.0	90	9.0

[a] Carried out at room temperature with 45 min stirring; analyzed by GC; error limit ± 2%.
[b] For structures of XII and XIII, refer to scheme 1.
[c] Unidentified products, and includes phenol and other brominated derivatives of phenol.
[d] Taken from reference [25].
[e] Lower loading level with 1.3 molecules/supercage (40 mg of IV).
[f] Solid-state bromination at higher loading level with 3.1 molecules/supercage (100 mg of IV).

Table 4
Percentage conversion and product distribution in bromination of chlorobenzene[a]

Solvent	Zeolite	% conversion	% yield of		
			X[b]	XI[b]	A[d]
CH_2Cl_2	nil	Nil	–	–	–
Hexane	nil	nil	–	–	–
Hexane	NaY[c]	50	10	65	25
Hexane	NaY	96	11	87	2.0
Hexane	NaY[d]	97	6.0	94	–
Hexane	NaX	58	–	86	6.0
Hexane	RbY	6.0	–	83	11
Hexane	CaY	10	–	100	–
Hexane	HY	nil	–	–	–

[a] Carried out at room temperature with 45 min stirring; analyzed by GC; error limit ± 2%.
[b] For structures of X and XI, refer to scheme 1.
[c] Reaction carried out with unactivated zeolite.
[d] Solid-state bromination.
[e] Unidentified products and includes chlorobenzene and other brominated derivatives of chlorobenzene.

2. Use of a nonpolar solvent, which ensures that the substrates are inside the cage/channels of zeolites.

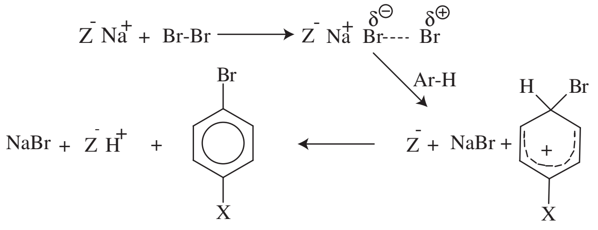
3. Predominant paraselectivity in bromination.

4. Absence of any difference in selectivity with variations in loading level, cation size, charge, acidity etc.

5. The marked difference in selectivity with phenol between nitration and bromination (particularly in solid state), which indicates that the two aromatic substitution reactions may follow different pathways in the presence of zeolites.

In their studies on the mechanism of bromination reactions, Smith *et al.* [18] have proposed two possible pathways that may be involved in brominations occurring within the zeolite cage. In one, a three-body process involving adsorption of both the substrate and bromine in close proximity to each other on the internal surface of the zeolite is proposed. Taking assistance from the sodium cation and the zeolite framework in the polarization of the bromine molecule and for removal of the proton from the aromatic ring, respectively, the reaction would result in NaBr, HY and the brominated aryl ring. It is relevant to note here that experimental and quantum chemical data show that the electrophilic reagent involved in bromination of benzene and toluene on NaY is more active than that on HY [26].

In a second alternative, initial reaction between zeolite and bromine produces a surface hypobromite species, which acts as the active brominating agent, with simultaneous generation of a Lewis acidic aluminum site. The surface hypobromite may be inaccessible to the more hindered ortho position. Both mechanisms envisage interaction between bromine and the zeolite framework. While adsorption of the substrate and bromine, as visualized in the first mechanism, is less probable, since the selectivity observed in bromination reaction is insensitive to activation/deactivation of the aryl ring, the second alternative of formation of surface hypobromite may play a major role. In addition, we also propose another mechanism (scheme 2) that does not involve any interaction with the framework, but involves assistance to the polarization of bromine coming from the charge-balancing sodium ion. This ensures the release of partially polarized bromonium ion (with its poor electrophilicity and greater ability to bear a positive charge), which is more stable and hence attacks the position of greater thermodynamic stability and the one which is the least hindered, namely, the para position. The assistance from the framework, we believe, comes after the rate-limiting step, by providing selective adsorption of HBr.



Z = Zeolite framework
X = -CH_3, -OH, -Cl, -$OCOCH_3$

Scheme 2. Mechanism of zeolite-assisted bromination of aromatic substrates.

The proposed mechanism also explains the difference in mechanism in zeolite-mediated nitration and bromination. Bromonium ion, the active species in bromination is less reactive and hence more selective in attacking the thermodynamically more stable para position, with both electron-releasing and electron-withdrawing substituents. This is in contrast to nitration [21], wherein ortho-nitrophenol is the predominant product in solid-phase nitration of phenol. This may be due to the more reactive nature of the nitrating species, which subsequently is less selective. It is also likely that the intramolecular hydrogen bonding between nitro and hydroxyl groups in ortho-nitrophenol may contribute to stabilize the intermediate, leading to the formation of the ortho-isomer.

4. Conclusions

Regioselective para bromination of aromatic substrates is observed in the presence of faujasite zeolites, which also catalyze the bromination of deactivated substrates, namely, chlorobenzene and phenyl acetate. NaY seems to be the ideal zeolite of choice and an active role for Na^+ is visualized in the proposed mechanism in which the less reactive bromonium ion (formed by polarization caused by Na^+ ion) attacks the thermodynamically more stable para position. The difference in selectivity in bromination and nitration of phenol is also explained on the basis of the differences in reactivity of the active species involved.

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